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Green and sustainable anticorrosive coating derived from waterborne linseed alkyd using organic-inorganic hybrid cross linker

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ABSTRACT

In near future, bio-based polymer coatings are expected to gradually replace the fossil oil based coating materials. However, extensive application of bio-based polymer is still a challenge because of its several limitations. The use of organic-inorganic hybrid cross linker is one of the interesting strategies used for the processing of highly crosslinked polymer coatings with improved mechanical and anticorrosive performance. Thus present work reports the preparation of organic-inorganic hybrid (OIH) cross linker using melamine formaldehyde (MF) and 3 isocynatopropyl triethoxy silane (IPTES). The structural characterization was carried out using various spectroscopic techniques, which provide ample evidence in favor of MF/IPTES cured alkyd formation. The impact of OIH cross linker on various properties like physico-mechanical, adhesion, thermal stability and anticorrosive properties was investigated systematically. The enhancement in aforementioned properties could be explained in terms of synergistic effect of s-triazine ring of melamine formaldehyde and IPTES.

1. Introduction

The use of renewable monomers for the synthesis of volatile organic compounds (VOC) free low molecular weight polymers has ignited interest among scientist and coating technologists to meet the challenges of unpredictable increase in the price fluctuations of fossil oil and its expected depletion in near future [1]. Among various renewable monomers, vegetable oils (VOs) due to their easy handling, abundant availability, sustainability, biodegradability, multifunctionality and low cost, have gained considerable scope for their application in the development of amphiphilic copolymers, composites, blends, plasticizers, and adhesives [2–4]. The vegetable oil based low molecular weight waterborne polymers have proved to be ecofriendly and VOC free polymers, find wide applications in different field of industries. Among these water borne alkyd (WA) owing to their low cost, VOC free, non-toxicity, non-flammability and low viscosity at high molecular weight find wide applications in the paints and coatings industries [5–7]. They gained importance in the field of anticorrosive coatings due to their eco-friendly nature [8]. Alkyds are also named as oil modified polyester, marked as one of the versatile class of polymers, have attracted the attention of coating technologists [9,10]. There are still many challenges associated with waterborne oil alkyds such as long drying time, unsatisfactory adhesion, and poor corrosion protection performance especially in alkaline environment [11]. Thus, in order to overcome these drawbacks, the application of organic-inorganic hybrid (OIH) cross linkers has been introduced which offer synergistic advantages of organic and inorganic phase in cross linkers [12,13].

The zirconium and titanium alkoxide have been widely used in coating industries as curing agents for polyester/alkyd coatings. Silicon coatings are often combined with zirconium-based materials to increase the adhesion on metallic substrates. The inclusion of zirconium alkoxide improved the coating performance in alkali medium [14]. However, the problem of compatibility in organic and inorganic phases still persist e.g. the dispersion of inorganic fillers in organic phase (matrix) and the presence of low content of organic functional groups cause leaching due to the lack of chemical (improper) interactions between the two phases [15,16]. However, silane coupling agents are generally used to overcome such problem. The use of coupling agents like silane induces interactions and enhances the bond strength between the organic (matrix), and inorganic (fillers) phases, that resulted in enhancement of coating performance [11].

Literature reveals that many workers have used silane and its derivatives for the synthesis of oleopolymers based OIH anticorrosive coating materials. For example, A. Ahmadi et al. studied the corrosion protective performance of hybrid silane coating [17]. Soucek et al. have reported Linseed oil (LO) and Soy oil (SO) based OIH films with improved mechanical properties [18,19]. Ahmad et al. synthesized vegetable oil derived polyurethane hybrid coatings with improved

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anticorrosive performance [20,21]. The development of high performance anticorrosive coatings using urea/polydimethylsiloxane based on different alkosiloxane was studied [22]. These investigations suggest that the use of silane cross linkers in sustainable polymer based OIH coatings exhibit improved physico-mechanical and corrosion resistance properties. However, the use of various ratio of OIH cross linkers in waterborne coating systems and their impact on thermal stability, mechanical and anticorrosive properties are still unexplored.

In view of this, here we report the use of MF/IPTES, an OIH cross linkers in various ratios for the preparation of waterborne linseed alkyd, as no literature is available on the use of MF/IPTES cross linker on physico-mechanical, thermal and anticorrosive properties of waterborne linseed alkyd coatings. The structure of OIH waterborne linseed alkyd was characterized using FTIR and NMR spectroscopic techniques. The detailed Physico-mechanical and anticorrosion performance of the OIH alkyd coatings were evaluated by standard methods. The polarization, electrochemical impedance spectroscopy and salt spray analysis of these coatings revealed that the inclusion of OIH crosslinker in waterborne linseed alkyd matrix resulted in high performance anticorrosive coating.

2. Experimental section

2.1. Materials and methods

The Linseed oil (LO) was supplied by Shanker Dyes and Chemicals (India); Bisphenol-A, phthalic anhydride, triethylamine, ethanol, and sodium hydroxide were procured from s.d. fine chemicals, Mumbai, India; and 3-isocyanatopropyltriethoxysilane (IPTES) and Dimethyltin dineodecanoate were obtained from Alfa Aesar UK. Sodium hydroxide (97%), sodium chloride (99%), triethylamine (99%), glycerol (98%), and hydrochloric acid (35 − 36%) were obtained from Fisher Scientific, New Delhi, India.

2.2. Synthesis

2.2.1. Synthesis of waterborne linseed alkyd (WLA)

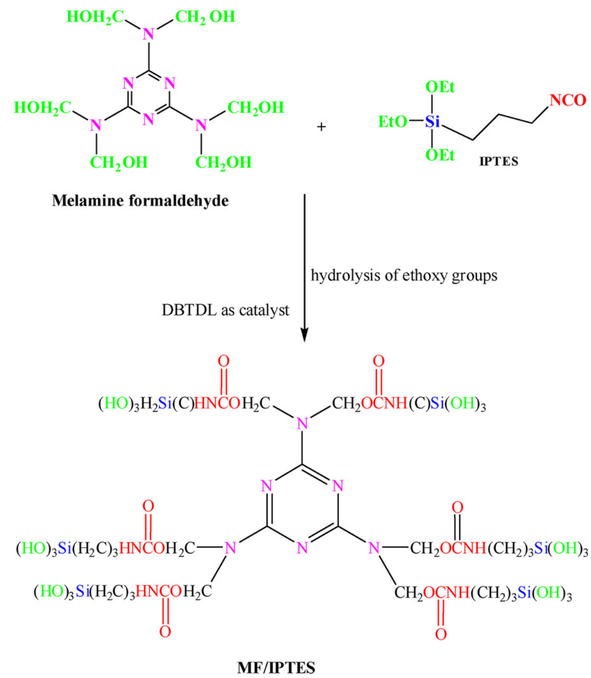
Waterborne linseed alkyd was synthesized by the reaction of linseed monoglyceride (LM) with phthalic anhydride in 1: 0.75 M ratio at 190 °C with continuous stirring (Scheme S1). LM and phthalic anhydride were taken in a three necked round bottomed flask equipped with a dean stark apparatus, nitrogen inlet, thermometer and magnetic stirrer. Bisphenol-A (0.5 mol) was dropwise added to the reaction mixture, the reaction was continue till the acid value reached to 60. The progress of the reaction was monitored by acid value taken at regular intervals of time. The terminal carboxyl groups were further neutralized by triethylamine (neutralizing agent) to reduce the acid value up to 30 followed by the dispersion of final product in water: ethanol blend (80:20) that led to the formation of WLA [11].

2.2.2. Functionalization of melamine formaldehyde by 3 isocynatopropyl triethoxysilane and their use for the curing of WLA

Melamine formaldehyde (MF) and IPTES were reacted in 1:6 M ratios using dibutyltin di laurate (DBTDL) as catalyst (0.5 wt % of DBDTL with respect to IPTES). The peak at 2260 cm^{-1} corresponding to NCO group disappeared after reacting with hydroxyl groups of MF. Later on, varying amounts of MF/IPTES cross linker (4 wt%, 5 wt% and 6 wt %) were added in alkyd matrix in presence of *p*-toluenesulfonic acid (PTSA) used as catalyst for 1 h. The reaction temperature was maintained between 100–120 °C. The reaction Scheme 1 represents the functionalization of MF with IPTES while Fig. 1 represents the crosslinking of WLA by MF/IPTES [23,24].

2.3. Characterizations

The structural characterization of LM, WL and MF/IPTES crosslinked WLA was carried out with the help of Fourier transform infrared (FT-IR), ^{1}H and ^{29}Si NMR. FTIR spectra were recorded on an IRAffinity-1 Shimadzu using ZnSe cell, the number of scan used in FTIR was 40 along with 4 number of resolutions. The ^{1}H NMR spectrum was recorded on JEOL GSX 300 MHz FX-100, using tetramethylsilane (TMS) as an internal standard. The ^{29}Si NMR spectrum of the hybrid sample was recorded on a Bruker 300 MHz (ProBHD-5 mm PABBO BB-, Pulprog-ZGPC]. The scanning electron microscopy (SEM) along with EDS was carried out on A FEI Quanta 200 F with Oxford-EDS system IE 250 X Max 80, Netherlands to study the morphology and elemental distributions in composite. The thermal stability of the hybrid coating was measured on EXSTAR TG/DTA 6000 at a scanning rate of 10 °C min^{-1} under N_2 in the temperature range 30–1000 °C at a heating rate of 10 °C min^{-1}.The Differential scanning Calorimetry (DSC) was done to record the glass transition temperature of the hybrid coatings using SII EXSTAR 6000, DSC620 at a heating rate of 10 °C min^{-1}. Microstructure analysis of the waterborne hybrid alkyd coated CS before and after cross hatch test as well as scratch test was performed on Lietz Optical Microscope (Model Metallux-3). The physico-mechanical properties like impact test, bend test and scratch hardness were investigated by standard methods [6]. The ASTM D 3359 crosshatch test was used to evaluate the adhesion of the coating with carbon steel substrate. The corrosion resistance performance of coated and uncoated samples was investigated in 3.5 wt. % HCl and NaOH solutions, at room temperature using potentiodynamic (PDP) and electrochemical impedance spectroscopy (EIS) micro Autolab type III (μ 3AVT 70,762 Netherland potentiostate/galvanostate). Salt spray test also was carried out in salt spray chamber according to the standard ASTM method (ASTM B117-09) to study the corrosion resistance performance of coatings under saline environment.



Scheme 1. Functionalization of MF with IPTES.

3. Results and discussion

The multifunctional OIH crosslinker was prepared through the chemical interaction of MF and 3 isocyanatopropyl triethoxy silane (IPTES). The bifunctional alkoxysilane contain isocyanate group, which react with hydroxyl groups of MF, resulting in the formation of MF/IPTES hybrid crosslinker. The influence of concentration of hybrid crosslinker on the properties of WLA coatings was investigated through